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Relations between the Melting Points and the Latent Heats of Fusion of the Metals

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RELATIONS BETWEEN THE MELTING POINTS AND THE LATENT HEATS OF FUSION OF THE METALS.

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In a lecture before this Institute in January, 1893, on "The Specific Heats of the Metals," I announced the fact that in the case of most of the metals whose latent heats of fusion were known, this quantity bears a simple relation to the heat required to raise the metal from absolute zero (— 273° C.) to its melting point. In most cases the former is one-third the latter. I even ventured to predict that the latent heat of fusion of gold was about 14 calories, and it has since been determined by Roberts-Austen as 16·3. Further, several latent heats have since been determined which conform to the above relation, and I have thought it opportune to collect these data and point out the limits of the relation, with some other observations which later thought on the subject has developed.

In the following table there is given, first, the heat required to raise 1 kilogram of the metal from the absolute zero to its melting point (using the most probable values for the specific heats and exterpolating to — 273°, for a discussion of which data reference is made to the paper already quoted); second, a simple fraction of this quantity and, lastly, the actually determined latent heats of fusion, the experimental errors of which are probably 5 to 10 per cent.:

Element.	*Heat Absorbed from — 273° C. to the Melting Point.*		*Latent Heat of Fusion (Experimental).*
Sodium	107·8	$\frac{1}{3}$ = 35·9	32·7
Aluminium	215·0	$\frac{1}{2}$ = 107·5	100·0
Potassium	54·9	$\frac{1}{3}$ = 18·3	15·7
Copper	145·3	$\frac{1}{3}$ = 48·4	43·0
Zinc	71·2	$\frac{1}{3}$ = 23·4	22·6
Gallium	21·9	$\frac{1}{1}$ = 21·9	19·2
Palladium	125·0	$\frac{1}{3}$ = 41·7	36·3
Silver	74·7	$\frac{1}{3}$ = 24·9	24·7
Cadmium	30·7	$\frac{1}{3}$ = 10·2	13·1
Tin	27·6	$\frac{1}{2}$ = 13·8	14·5
Platinum	83·4	$\frac{1}{3}$ = 27·8	27·2
Gold	45·3	$\frac{1}{3}$ = 15·1	16·3
Mercury	7·5	$\frac{1}{3}$ = 2·5	2·8
Lead	17·7	$\frac{1}{3}$ = 5·9	5·4
Bismuth	14·4	$\frac{1}{1}$ = 14·4	12·4

Of the fifteen cases, the relation in eleven cases is one-third (in almost every case within the limits of the experimental errors); in two cases the fraction is apparently one-half, and in two cases unity. That for ten cases the ratio should be so uniform, with latent heats ranging from less than 3 to nearly 50, is an indication of some intimate connection between these physical constants of the elements.

Regarding the exceptional cases, it occurred to me that aluminium, tin and bismuth are known to act anomalously in many relations, as if their molecular structures were different from that of the other metals. (We have no data from which to discuss Gallium in these relations.) For instance, in lowering the freezing point of other metals, aluminium is known to act as if its molecular formula were double that of other metals in the molten state. In Pictet's observation of the connection between the melting point, coefficient of expansion and atomic volume of an element, bismuth and tin are among the chief exceptions.

[Pictet's rule is that the melting points of the elements (T, in absolute degrees) are, in many cases, inversely proportional to their coefficient of expansion by heat (a = linear expansion 0° to 100° C.) and to the relative distance of their atoms apart ($\sqrt[3]{V}$, where V is the atomic weight divided by the specific gravity, or atomic volume) for which Pictet's relation is expressed by

$$T \cdot a \cdot \sqrt[3]{V} = 4{\cdot}5$$

or

$$T = \frac{4{\cdot}5}{a \cdot \sqrt[3]{V}}.$$

In fact, the products of these three quantities are not exactly equal, but vary between 4 and 5, the reason being, doubtless, that the average specific gravity and rate of expansion from — 273° to the melting point varies somewhat from the gravity at 20° and rate of expansion at 0° to 100° as used in his calculations.]

As already mentioned, bismuth and tin were Pictet's chief exceptions, and since they were anomalous in regard to their latent heat relations, I was led to compare these several relations among themselves, and to the following chain of reasoning: Since the atomic heats of the elements (specific heat into atomic weight) at 20° to 100° are, by Dulong and Petit's law, approximately equal to 6·4, then, assuming that the average specific heat from — 273° to the melting point does not vary much from the figure for 20° to 100°, the heat in atomic weight of a metal at its melting point is approximately 6·4 T; and, assuming the relation between the latent heat of fusion and the total heat in the metal at its melting point as $\frac{1}{3}$, the latent heat of fusion of an atomic weight of a metal becomes approximately 2·1 T.

But we can at once connect this expression with Pictet's rule, and write:

$$L = 2{\cdot}1\ T = \frac{4{\cdot}5 \times 2{\cdot}1}{a \cdot \sqrt[3]{V}} = \frac{9{\cdot}5}{a \cdot \sqrt[3]{V}},$$

where L is the latent heat of fusion of an atomic weight of the metal.

To test the validity of this expression (which, for reasons already explained, cannot claim exact accuracy), we will take Pictet's values for $a \cdot \sqrt[3]{V}$ (which are based on the best available data) and make the calculation for the metals whose latent heat of fusion and coefficient of expansion are both known.

	$L = \frac{9\cdot5}{a \,.\, \sqrt[3]{V}}$	$\frac{L}{At.\ Wt.}$ = *for 1 kilo.*	*Latent heat experimentally obtained.*
Aluminium	1,900	70·4	100·0
Copper	3,006	46·2	43·0
Zinc	1,561	24·6	22·6
Palladium	3,832	36·1	36·3
Silver	2,541	23·5	24·7
Cadmium	1,253	11·1	13·1
Tin	1,712	13·7	14·5
Platinum	5,106	26·3	27·2
Gold	3,035	15·5	16·3
Mercury	654	3·3	2·8
Lead	1,284	6·2	5·4
Bismuth	2,777	13·4	12·4

Excepting aluminium, the coincidences are so close in the case of all the others that the calculated values in every case fall within the permissible limits of experimental errors, and it must be remembered that the above table contains *all* the metals for which the data are at present available. The non-metal sulphur expands so irregularly that no calculation can be made for it.

The closeness of the above coincidences may lead us to apply the formula to those other elements whose coefficients of expansion are known, but whose latent heat has not yet been determined, and thus to predict approximately the probable value of their latent heat of fusion.

	Calories.
Magnesium	58·
Pure iron	69·
Cobalt	68·
Nickel	68·
Selenium	13·
Ruthenium	46·
Rhodium	52·
Indium	8·
Antimony	16·
Tellurium	17·
Osmium	35·
Iridium	28·
Thallium	5·8

In the case of those other elements whose coefficients of expansion and specific heat are both unknown, the latent heats of fusion may be predicted, approximately, simply from the melting point, by using the relation $L = 2\cdot1\ T$.

The above comparisons, however, have shown that the dependence of the atomic latent heat of fusion on the absolute temperature of the melting point, or on the total heat in the metal at its melting point, is less exact than the dependence on the coefficient of expansion and atomic volume, and we should give the latter relationship preference in predicting unknown latent heats.